

NASA GRANT NAGW 0-3569 FINAL REPORT

Under the above grant research was funded in the following areas:

1. Pallasites: Rare earth element measurements in phosphates to determine if all pallasites fit into only two trace element groups. This work has been completed. One manuscript has been published in the journal *Nature* (Davis & Olsen, 1991), and a second manuscript is being prepared to include an additional large body of measurements which have just been completed.
2. IIIAB irons: To complete work on the only known silicate inclusion in a IIIAB iron meteorite, Puente del Zacate, discovered and reported (Olsen et al, 1992). This work has been completed and a manuscript has been written and submitted for publication (Olsen et al, in prep1).
3. IIIAB irons: To continue the search for ^{53}Cr excesses in IIIAB iron meteorite phosphates. A part of this work has been completed (Hutcheon & Olsen, 1991; Hutcheon et al, 1992), however, there is still more to be done. It has not been entirely completed because a critical collaborator, I. Hutcheon, changed employment during the course of the project. He will be able to continue this project in his new location during 1996.
4. IIIAB irons: To complete the identification of the phosphate minerals in IIIAB iron meteorites and try to determine the phase relations and chemical history of trace element distributions during the core formation process. Work on this has been largely completed and preliminary results have been reported (Olsen & Steele, 1993; Olsen & Steele, 1994). The final work is being assessed prior to preparation of a manuscript for publication.
5. IIE irons: To complete work on the unique silicate assemblage in the IIE iron meteorite, Watson. Work on this was completed and a paper published in the journal, *Meteoritics* (Olsen et al, 1994).
6. Ungrouped irons: A partially devitrified silicate glass inclusion has been found in the ungrouped iron meteorite Mbosi. Preliminary work on this has been reported (Olsen et al, 1995). All the work on this has been now completed and a manuscript has been prepared and submitted for publication (Olsen et al, in prep2).

DETAILED DISCUSSION OF ABOVE NUMBERED ITEMS

1. PALLASITES — ION MICROPROBE MEASUREMENTS OF REE IN PHOSPHATES

In this work we prepared a total of 72 polished sections from 34 pallasites on loan from Arizona State University, the American Museum of Natural History, the National Museum of Natural History, the University of Chicago and the Field Museum of Natural History.

Each of the sections was searched for the presence of phosphate phases. This required slow, careful scanning on a scanning electron microscope, micrometer by micrometer, using back scattered electron detection to locate any small phosphates interstitial to olivine; they are very

difficult to locate optically in a polished section. We previously determined, on the basis of sections of ten of these pallasites that eight of them contain phosphates characterized by enrichments in HREE over LREE, while two of them contain phosphates characterized by the opposite, LREE enriched over HREE. These results were published in Davis & Olsen, 1991. Phosphates have been found in an additional 13 pallasites over and above the ten originally studied. Ion microprobe measurements have been completed on these. Two of these pallasites are new finds (Vermilion and Yamato-8451) which contain moderately abundant pyroxenes (pyroxenes are rare in pallasites). Up to this point only Eagle Station contained pyroxenes large enough to be measured by ion microprobe.

The completed measurements on all 23 pallasites indicate more complex patterns of REE enrichments than described above. Some of these additional pallasites fall into the two REE groups previously determined, however, several of them have unique REE enrichment patterns. We are currently working on interpretations of these measurements and patterns and will prepare a manuscript for publication.

2. IIIAB IRONS — PUENTE DEL ZACATE SILICATE INCLUSION

We discovered a silicate inclusion in the IIIA iron meteorite, Puente del Zacate. It is the only known member of this group to contain a silicate inclusion (Olsen et al, 1992). Other members of the IIIAB group frequently have Fe-rich phosphate inclusions; the only silicate occurrence heretofore known in them consists of rare, trace occurrences of tridymite associated with the Fe-rich phosphates.

The silicate inclusion is a 7 mm fragment contained within a troilite nodule. Because of its rarity we attempted to do as much as possible with a very small chip of it, preserving most of it for future studies by others. Electron microprobe measurements on the individual minerals, scanning electron microscopy, optical microscopy, ion microprobe measurements on the individual minerals, bulk oxygen isotope composition were all obtained on the single chip.

The silicate assemblage in Puente del Zacate consists of olivine (Fa4), low Ca pyroxene (Fs6/Wo1), high Ca pyroxene (Fs3/Wo44), plagioclase (An14/Or4), chromite, troilite and graphite.

The oxygen isotope composition is $^{17}\delta\text{O} = +1.08$, $^{18}\delta\text{O} = +2.35$. In the three oxygen isotope diagram this plots on the fractionation line with the IIIAB irons and the HED-mesosiderite-main group pallasite (AMP) association, however, the composition is not consistent with physical trapping of achondritic material, since it is displaced along the fractionation line by about 1‰ in $\delta^{18}\text{O}$ from achondritic silicates of comparable mineralogy. The whole rock isotopic composition of Puente del Zacate silicates lies within the range observed for chromite and phosphates from other IIIAB irons.

This silicate inclusion presented unique problems in analysis. Initially we obtained images

of portions of the inclusion and performed image analysis on them in order to determine the mineralogical mode. This mode, combined with ion microprobe measurements of the individual minerals, permits calculation of the whole rock REE and other trace element contents. The mode determined by image analysis (reported in Olsen et al, 1992) was found to be incorrect, due to the large percentage of the section's area that consisted of holes, many of them filled with graphite. A new mode was obtained by doing areal analyses with the electron microprobe.

From these results new whole rock trace element patterns have been calculated. The silicate has a flat, chondritic REE pattern and the mineralogy is exactly like that of silicate inclusions in many IAB iron meteorites. Silicates in IAB irons are commonly high in pyroxenes and plagioclase, low in olivine, and have minor element contents that, up to now, have been considered unique. The Puente del Zacate silicates are identical in their minor element compositions to the IAB silicates. On the basis of oxygen isotope systematics the IAB and IIIAB irons are not related to each other. Mineralogically, however, they share their unusual mineralogy, a mineralogy not known in any other meteorite type.

A manuscript has been prepared and submitted for publication.

3. IIIAB IRONS — THE SEARCH FOR ^{53}Cr EXCESSES

We have already obtained a body of ion microprobe data on ^{53}Cr excesses in phosphate minerals in Cape York (IIIA), El Sarnal (IIIA), Grant (IIIB), and Bella Roca (IIIB) (Hutcheon & Olsen, 1991; Hutcheon et al, 1992). ^{53}Cr excesses were found in all of these in the range of 6‰ to over 30‰ and are correlated with the Mn/Cr ratio. These data taken together indicate *in situ* decay of ^{53}Mn after the metal core was separated within the parent body, and confirm that isotopes such as ^{26}Al , ^{107}Pd and ^{129}I were freshly synthesized and injected into the Solar System as it was forming. The time differential implied by the Mn-Cr isotope systematics indicates an approximate 6 million year differential in closure between these members of the IIIAB group. This suggests they are derived not from a single parent body but more than one parent body.

This study depends on the presence of phosphate minerals with at least several percent of Mn and no detectable Cr ($\ll 100$ ppm). If a phosphate has very high Mn, *i.e.* > 10 wt%, it is possible to analyze it on the ion microprobe at the University of Chicago. If, however, it has a lower Mn content (≤ 2 wt%), it requires an ion microprobe with higher sensitivity. Until now we have analyzed all the samples that can be analyzed on the ion microprobe at the University of Chicago. Those with lower Mn have been analyzed in collaboration with Dr. Ian Hutcheon at Caltech. Dr. Hutcheon has changed positions and has moved to the Lawrence-Livermore Laboratory. He is still interested in collaboration on this project and will be able to continue it on the ion microprobe at Livermore during 1996. Thus, work on this project is temporarily stalled until our low Mn samples can be analyzed at Livermore.

In the meantime electron microprobe searches have been completed on phosphates in the Chupaderos (IIIB) and Mount Edith (IIIB) irons. Chupaderos has several phosphate occurrences

to be analyzed by ion microprobe and added to the present data set. Mount Edith has abundant phosphates, however, they all carry Cr levels too high to be worth analyzing. Additional samples of Cape York are in hand but have not yet been searched for likely phosphates.

4. IIIAB IRONS — PHOSPHATE MINERALOGY

Work on this aspect of our grant has almost been completed except for x-ray diffraction measurements on several of the minerals discovered in the course of the work (Olsen & Steele, 1993; Steele et al, 1991; Steele et al, in press). It is probable that phosphates in IIIAB irons ought to be equilibrium assemblages because of the very low cooling rates of these irons. Terrestrial phosphate assemblages are notoriously metastable because they form mainly by a series of low temperature reactions in the presence of ample water (usually in pegmatites), or in sedimentary environments under wet, diagenetic conditions. Phase equilibrium studies in phosphate systems, especially Fe-rich phosphates, are difficult to pursue and only a few systems have been studied. Because of the reaction of FeO and phosphorus with common reaction vessels, phase equilibrium studies of the Fe-rich phosphates are almost nonexistent. It is probable that IIIAB Fe-rich phosphates forming in a dry core environment might offer insights into equilibrium assemblages of these anhydrous phosphates.

We have found these phosphates in the IIIAB irons we have studied:

Group 1 phosphates

Graftonite (or its polymorph Sarcopside)	$(\text{Fe,Mn})_3(\text{PO}_4)_2$ Fe>Mn
Beusite	$(\text{Mn,Fe})_3(\text{PO}_4)_2$ Mn>Fe
Johnsomervilleite	$\text{Na}_2\text{Ca}(\text{Fe,Mn})_7(\text{PO}_4)_6$ Fe>Mn
New mineral #1	$\text{Na}_2(\text{Fe,Mn})_8(\text{PO}_4)_6$ Fe>Mn
New mineral #2	$\text{K}_2(\text{Fe,Mn})_8(\text{PO}_4)_6$ Fe>Mn

Group 2 phosphate

Maricite	NaFe PO_4
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Cape York assemblage

Buchwaldite	NaCaPO_4
Maricite	NaFe PO_4
Uncharacterized	Phosphate
Uncharacterized	Phosphate

Group 1 phosphates above are the ones that occur most frequently in IIIAB irons.

Graftonite and beusite are isostructural and they do not coexist within a single meteorite. If graftonite is present, then beusite does not occur. If beusite is present then sarcopside (structurally different) can be present.

Johnsomervilleite appears in most occurrences, coexisting with graftonite or beusite + sarcopside. At the time this grant was originally proposed by us we did not understand which of the possible Na-bearing phosphates were present. From our knowledge of terrestrial phosphates we had determined only that some phosphates akin to either dickinsonite, arrojadite or fillowite

were present. During our period of funding we have determined that it is johnsomervilleite, which is chemically (and probably crystallographically) related to fillowite. Fillowite is $\text{Na}_2\text{Ca}(\text{Mn,Fe})_7(\text{PO}_4)_6$ with $\text{Mn} > \text{Fe}$. The crystallography of terrestrial johnsomervilleite has never been adequately determined; its x-ray pattern and structure have been deduced to be the same as the terrestrial fillowite structure, which is known. The existing x-ray data on terrestrial johnsomervilleite are based on a sample that was so altered it gave initial inferior results; it was then heated in air to recrystallize it and then x-rayed again, a process we believe to be flawed considering that the iron in it must have largely oxidized during the heating process. We have extracted a grain of meteoritic johnsomervilleite large enough for x-ray work, however, it had been so totally shocked on the parent body (presumably during breakup) that it gave no x-ray pattern. Subsequently another sample large enough for x-ray work was extracted and single crystal x-ray data were collected to determine the structure. Unfortunately the extracted grain consisted of three very small crystals and the single crystal diffraction data were useless. We shall continue to seek a single crystal in order to obtain a single crystal pattern. In the meantime, we have made Gandolfi powder diffraction measurements on the multiple crystal grains we do have. Its pattern differs from the published pattern of the terrestrial johnsomervilleite, mentioned above. It has a different cell size. The pattern does, however, index perfectly in the rhombohedral space group, R. Most of the phosphates related to johnsomervilleite are in this space group.

The two new phosphates in Group 1 above have been encountered repeatedly in IIIAB irons. We have located some grains of each of them large enough for x-ray work and intend to obtain structural information. We believe they will have structures different from that of johnsomervilleite but probably related to it.

Maricite occurs in only a few IIIAB irons, where it is the only phosphate mineral present. It coexists with tridymite and chromite. Ion microprobe work on it shows it to be virtually free of trace elements at detection limits of approximately 1 ppm for most elements; this indicates it must have formed within the core by an oxidation event, deriving its phosphorus from the metallic phase.

The Cape York Group is a unique group of Na-rich phosphates known only in the Cape York IIIA iron. Of the several phosphates found in it only buchwaldite occurs in grains large enough for complete characterization.

The presence of Na-bearing phosphates in all groups of IIIAB irons is puzzling. Na is a volatile element and its presence in a core situation would not be predicted. Possible explanations are discussed by Olsen & Steele (1994). They conclude that solubility in sulfide may control the presence of trace amounts of Na along with Ca and Mn in the core, but not Mg, Si and Al, which are abundant elements in planetary chemistry, but are not detected in the core phosphates. This point will be pursued during subsequent work.

5. COMPLETION OF STUDY OF THE WATSON IIE IRON METEORITE

Watson is an especially important IIE iron meteorite with an extraordinarily large inclusion of melted, metal-depleted H-group chondrite contained within it. During the course of this funding we have completed all work on it and a paper was prepared and published (Olsen et al, 1994). The work includes: petrography, scanning electron microscopy, mineralogy, bulk trace elements by INAA and RNAA, noble gas measurements, oxygen isotope composition, metallography, wet chemical composition. It involved a total of 14 researchers from eight different institutions, led by the P.I. of this grant. It was a relatively smooth consortium effort. The unique nature of Watson deserved this kind of attention. Watson silicate is clearly a melted and [then] recrystallized mass of an H-group chondrite contained in IIE metal when the metal itself was molten. Watson belongs to the “young” group of IIE irons, that is, a silicate assemblage that records a closure age of 3.7 Ga, as opposed to other IIEs which give ages of 4.5 Ga. Watson silicate gives a cosmic ray exposure age of 8 Ma, which is the most frequent exposure age of the H-chondrites, and very different from the peak exposure age of irons, 900 Ma. This firmly establishes the genetic relationship between H-chondrites and the IIE irons. Watson fills in a gap in the sequence of events that took place on the surface of the parent body, from incorporation of chondrule-bearing unmelted chondrite material (in the IIE Netschaëvo) to the highly fractionated silicates seen in such IIEs as Kodaikanal.

6. THE UNGROUPED IRON, MBOSI

Four ungrouped iron meteorites have one common property shared with the IIF irons and the Eagle Station trio of pallasites; they all have Ge/Ga ratios >10 . A Ge/Ga ratio >10 cannot be explained by igneous fractionation in a parent body core (Kracher et al, 1980). None of these ungrouped irons was known to have silicate inclusions, however, the P.I. discovered that one of them, Mbosi, contains very small silicate blebs within the metal (Olsen et al, 1995). The silicate is partially devitrified glass. Individual minerals cannot be resolved, however, a bulk x-ray powder diffraction pattern of the silicate shows the principle diffraction peaks of pyroxenes and plagioclase. Two of the inclusions contains, in addition, single grains of silica. The silicate inclusions appear to have been almost totally melted, the silica, because it is more highly polymerized than the other silicates, did not completely melt before the system quenched. The bulk composition of the silicate inclusions was determined by electron microprobe and the bulk trace element and REE pattern determined by ion microprobe. In addition, the oxygen isotope composition was measured.

The most important result of this study comes from the oxygen isotope composition. In the three-isotope diagram the bulk Mbosi point plots close to the C3 mixing line. A line joining Mbosi with the Eagle Station trio composition has a unit slope mixing line parallel to the C3 mixing line and offset from it by approximately 1‰ in ^{18}O . Furthermore, the Mbosi-Eagle Station line passes through the point for the anomalous iron, Bocaiuva, which is an iron related to the IIF irons, and it also has Ge/Ga >10 . Thus, three metal-rich meteorites, all characterized by the anomalous property of Ge/Ga >10 , lie on a mixing line parallel to the C3 line. Thus they appear to

have a similar origin and mixed from a region in the primitive nebula characterized by a distinct oxygen composition which is close to that of the primitive carbonaceous chondrites. Thus, an explanation for the anomalously high Ge/Ga ratio, an explanation which has eluded us so far, must be contained in the particular nebular origin of these irons.

A paper has been written on these results and has been submitted for publication.

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